

SALINE WASTEWATER PROCESSING

5 The present invention relates to removal of dissolved solids from inorganic saline wastewaters to recover a number of valuable waste products and to minimise disposal costs and potential environmental impacts. One aspect of the invention relates to reduction of the bulk of dissolved solids in particular types of wastewater and another aspect of the invention is to produce a range of valuable salt mineral and slurry products from such wastewaters.

15 Agricultural, mining, industrial and municipal activities in arid and semi-arid regions of Australia and other countries produce large quantities of saline wastewaters which contain significant amounts of dissolved salts and are considered potentially dangerous to the environment. Currently most of these liquid wastes are disposed of through the use of retainment, filtration and evaporation ponds as well as discharged into natural waterways. Pollution of waterways occurs due to the latter method of disposal and the retainment, filtration and evaporation ponds currently in use result in large volumes of waste and minimal revenue from any commercially saleable salt chemicals recovered.

It is consequently an object of the present invention to disclose a method of treatment for wastewaters rich in Sulphates, Potassium and Magnesium which process overcomes one or more of the disadvantages with existing processing methods or at least it provides an alternative.

According to the present invention there is disclosed a process for reduction of the dissolved salt content and volume of saline inorganic wastewaters having at least five (molar) percent Sulphate (SO_4) content; being one or more of the following water types; Na-(Mg)-Cl-(SO_4), Na-(Mg.K)-Cl-(SO_4), Na-(Mg)-Cl-(SO_4), Na-Cl, Na-(Mg)-Cl, and having an Mg/2K (molar) ratio greater than 1.4 comprising the steps of;

(a) placing the feed solution in a preconditioning pond to precipitate impurities and raise the specific gravity to at least 1.15;

(b) shifting the feed solution to an evaporation pond and continuing evaporation to precipitate NaCl until the solution reaches a specific gravity of between 1.23 and 1.25;

(c) cooling the brine resulting from the aforementioned steps to between Zero and minus

Five Degrees Celsius and then dewatering the solution to separate Mirabilite crystals.

5 In its most basic form above described the present invention gives Halite, Mirabilite and a filtrate suitable for further processing in accordance with the present invention to produce Potassium Chloride, Epsomite , a 40% slurry of Magnesium Hydroxide and
10 other products. The Mirabilite produced in accordance with the process of the present invention may also be further processed so as to produce Thenardite and Potassium Sulphate. Production as lastmentioned in accordance with the processes disclosed in the present
15 invention not only gives saleable products but drastically reduces the volume of feed solution.

Whilst contemporary thinking has resulted in attempts to evaporate wastewater in order to reduce its volume
20 and produce useful products the present invention discloses a comprehensive scheme for multiple evaporation and cooling in order to achieve a range of useful products.

25 By way of illustration a number of schemes for treatment of wastewater in accordance with the present invention will be hereafter described with reference to the abovementioned diagrams in which;

Figure 1 is a flow chart indicating the basic steps through which an appropriate feed solution may be taken so as to give a number of products. The flow chart additionally indicates inter-relationships between the production of the various products;

Figures 2 to 3,4,5 and 6 are further flow charts showing separately the paths in accordance with the present invention necessary to produce Thenardite, Potassium Sulphate, Potassium Chloride, Epsomite and a Magnesium Hydroxide slurry respectively and;

Figure 7 is a table indicating the appropriate thermodynamic conditions and other parameters which the applicant has determined by experimentation are necessary for production of various products in accordance with the present invention.

Feed solutions considered generally suitable for the process disclosed herein are those inorganic saline wastewaters with more than 5 mol.% SO_4 and with the following chemical characteristics:

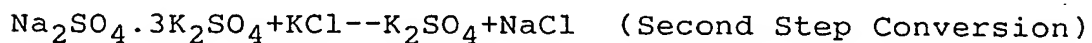
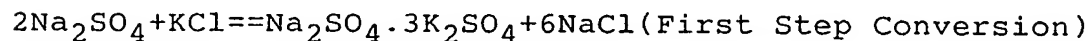
<u>Ratio</u>	<u>Water Types</u>
Mg/2K mol. \leq 3	Na-(Mg)-Cl-(SO ₄) & Na-(Mg.K)-Cl-(SO ₄)
3 < Mg/2K mol. < 6	Na-(Mg)-Cl-(SO ₄) & Na-Cl
5 Mg/2K mol. \geq 6	Na-(Mg)-Cl

For production of Mirabilite (Na₂SO₄.10H₂O) and Thenardite (Na₂SO₄), as shown in FIG. 2, the feed solution is first pre-concentrated by solar evaporation to about SG(Specific Gravity)=1.20 and then transferred to an evaporation pond and concentrated by evaporation to SG=1.25; maximum SG at this stage should not exceed 1.29. In summer the concentrated brine is naturally evaporated to $1.30 \leq SG \leq 1.32$ and dewatered to produce a salt slurry which is then dissolved in fresh water, cooled down to between zero and minus five Degrees Celsius and dewatered to produce Mirabilite product.

The route for summer Mirabilite production, as shown in FIGS 1 & 2, can be shortened by applying artificial cooling to filtrate bittern, after initial evaporation, followed by dewatering to produce Mirabilite product. As a cost-effective alternative, in winter, the resultant concentrated brine can be naturally cooled to temperatures down to between zero and minus five Degrees Celsius then dewatered to produce Mirabilite product.

The Mirabilite thus produced is then dehydrated to Thenardite in several ways. The first and simplest way is to wash the Mirabilite crystals with an appropriate washing liquor, then dewater and dry to produce Thernardite product; the second way utilises a chemical replacement method for obtaining higher productivity involving first the dissolution of Mirabilite by hot steam followed by reaction with Halite and normalisation of the mixture to forty Degrees Celsius then dewatering and drying to obtain Thernardite product. The third way utilises addition of Ethanol to Mirabilite crystals to decrease the solubility of the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system and hence increase Na_2SO_4 productivity. The Ethanol in the filtrate is then recovered by distillation.

For production of Potassium Sulphate (K_2SO_4), as shown in FIG. 3, the Mirabalite product is first dissolved by hot steam, and then subjected to two-step conversion with KCl according to the following reactions:



The first conversion is accomplished by reacting KCl with solution rich in Mirabilite through continuous mixing for thirty minutes at thirty five Degrees

Celsius and then dewatering it to produce Glasserite crystals in NaCl base solution. For the second conversion, the Glasserite crystals are reacted with KCl through continuous mixing for thirty minutes at
5 fifty Degrees Celsius and the mixture is then cooled down to ambient temperature (twenty-twenty five Degrees Celsius) to obtain K_2SO_4 crystals in the NaCl base solution, which is then dewatered and dried to produce
10 the final K_2SO_4 product. As shown in FIGS 1 & 3, the filtrate biterms from the conversion reactions are recycled to maximise Potassium recovery.

For production of Potassium Chloride (KCl), as shown in
15 FIG. 4, the biterms from dewatering of Mirabilite and Epsomite slurries are first artificially evapoarated to SG=1.36, and left to reach ambient temperature (twenty - twenty five Degrees Celsius) then dewatered. The resultant carnallite mixture is subjected to sequential
20 flotation and the solids subsequently separated by centrifuge and dried to produce the final Potassium Chloride product.

For production of Epsomite ($MgSO_4 \cdot 7H_2O$), as shown in
25 FIG. 5, the filtrate biterm from the Mirabilite production stream is evaporated to separate the Halite impurity and to increase the biterm density to $1.28 < SG \leq 1.30$, artificially cooled to between zero and minus

five Degrees Celsius then dewatered to produce Epsomite crystals. To increase recovery the Epsomite crystals thus produced are redissolved in hot water, evaporated to $SG=1.30$, and left to gradually normalise with ambient temperature (twenty - twenty five Degrees Celsius) then dewatered and dried to produce the final Epsomite product.

For production of $Mg(OH)_2$ slurry, as shown in FIG. 6, the bittern filtrate from the KCl production stream is first diluted with fresh water to $1.05 < SG \leq 1.10$, then reacted with Lime (CaO) by rapid stirring in a tank. Thickening by using a slow mixer and subsequent dewatering gives the final $Mg(OH)_2$ slurry product.

Depending upon the chemical composition of the feed solution the scheme of the present invention contemplates that removal of additional salts will be possible by further processing of the filtrate from the dewatering steps of the Mirabilite production.

The following specific examples will more precisely illustrate the invention and teach the procedure presently preferred for removal of dissolved solids as waste products based on the integrated processing schedule described herein.

EXAMPLE 1

One thousand litres (about 1cu.m) of a single waste stream from a saline groundwater source, which analyzed
5 as 882 mg/l Calcium, 3159 mg/l Magnesium, 10350 mg/l Sodium, 4692 mg/l Potassium, 25 mg/l carbonate and bicarbonate, 6720 mg/l Sulphate, 18939 mg/l Chloride, and measured 50g/l total dissolved solids (TDS), was
10 first evaporated in a pre-concentration pond to SG=1.20, which produced some impurities (mainly Gypsum) then further concentrated by evaporation to SG=1.25 which produced 25kg of Halite salt. The summer process route shown in FIG. 2 was followed in this case to
15 produce a Mirabilite slurry, which was subsequently dissolved by hot steam. Halite was then added to reach an NaCl to Slurry weight ratio of 3.8 : 1 and then the solution was brought to forty Degrees Celsius by continuous mixing. Following dewatering and drying of
20 the solids about 8kg Na_2SO_4 with 96% purity was produced. The Na_2SO_4 recovery was 93%.

The filtrate bittern from Thenardite production was then subjected to the processing steps shown in FIG. 5
25 to produce about 6kg of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ with 74% purity. The $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ recovery was 65.5%.

The filtrate bitters from Thenardite and Epsomite production were then mixed and subjected to processing steps indicated in FIG. 4 to produce about 5kg of KCl. The KCl purity was 90.3% and recovery was 58%.

5

10

15

The bulk of KCl thus produced was then used for production of K_2SO_4 salt by reacting it with dissolved Mirabilite through the two-step conversion process outlined earlier and shown in FIG. 3. Accordingly, for the first conversion a mixture with an $Na_2SO_4 \cdot 10H_2O$ to KCl to H_2O weight ratio of 1 : 1.82 : 3.0 was continuously mixed for 1/2 an hour at thirty five Degrees Celsius and then dewatered to produce Glasserite crystals in NaCl base solution.

20

For the second conversion a mixture with a Glasserite to KCl to H_2O weight ratio of 1 : 0.25 : 0.8 was continuously mixed for half an hour at fifty Degrees Celsius and then cooled down to twenty five Degrees Celsius. Following dewatering and drying about 6kg of K_2SO_4 with 96% purity was obtained. The K_2SO_4 recovery was 60% and the total Potassium recovery for this example was more than 80(wt)%.

25

By following the processing steps indicated in FIG. 6, the filtrate bittern from production of KCl was first diluted with fresh water to SG=1.10 and after adding a

near equal amount (by weight) of industrial grade lime powder (85wt% CaO) the mixture was drastically stirred for about 15 minutes. The solution was then thickened by slow mixing and after separating the waste solution dominated by CaCl_2 a 5kg slurry with 40(wt)% $\text{Mg}(\text{OH})_2$ was obtained. The analysis of this slurry indicated less than 5% NaCl in solution.

Overall, in this example, 92(wt)% of the total dissolved solids were extracted as impurities, Halite, Mirabilite, Thenardite, Epsomite, Potassium Chloride and Potassium Sulphate salts and as Magnesium Hydroxide slurry. Apart from a minor quantity of CaCl_2 -rich waste solution which resulted from $\text{Mg}(\text{OH})_2$ slurry production the bulk of filtrates from solid-liquid separation stages are recycled within the process system either as a feed or as an additive for comprehensive utilisation of the saline wastewater.

EXAMPLE 2

In another run similar to that of EXAMPLE 1 the same feed solution was subjected to the process route for Thenardite production as shown in FIGS 1 & 2. However following Halite replacement and dewatering the Na_2SO_4 crystals were redissolved in fresh water and

recrystallised by cooling to zero Degrees Celsius. The
Na₂SO₄ recovery rate was 98% although the Na₂SO₄
productivity remained the same as in EXAMPLE 1
(8kg/cu.m.). For production of Epsomite and KCl salts,
5 the procedures in EXAMPLE 1 were followed. However, for
the production of K₂SO₄ the weight ratio for
Na₂SO₄.10H₂O to KCl to H₂O in the first conversion was
changed to 1 : 0.35: 0.5. The procedure for mixing,
10 dewatering and the second conversion was the same as in
EXAMPLE 1. In this case the K₂SO₄ recovery was 78%,
while the K₂SO₄ purity remained at 96%.

It will be apparent to those familiar with saline
15 processing that the present invention offers a
comprehensive and highly flexible processing scheme for
recovery of the salt products from inorganic saline
wastewaters. The flexibility of the system relates to
its ability to recycle both the solids and the
20 filtrates to produce different useful and saleable
combinations of available waste products according to
feedstock characteristics and product market demand.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

- 5 1. A process for reduction of the dissolved salt
content and volume of saline inorganic wastewaters
having at least five (molar) percent Sulphate (SO_4)
content; being one or more of the following water
10 types; $\text{Na-(Mg)-Cl-(SO}_4\text{)}$, $\text{Na-(Mg.K)-Cl-(SO}_4\text{)}$, Na-
 $\text{(Mg)-Cl-(SO}_4\text{)}$, Na-Cl , Na-(Mg)-Cl , and having an
 Mg/2K (molar) ratio greater than 1.4 comprising the
steps of;
- 15 (a) placing the feed solution in a
preconditioning pond to precipitate impurities
and raise the specific gravity to at least 1.15;
- 20 (b) shifting the feed solution to an evaporation
pond and continuing evaporation to precipitate
NaCl until the solution reaches a specific
gravity of between 1.23 and 1.25;
- 25 (c) cooling the brine resulting from the
aforementioned steps to between Zero and minus
Five Degrees Celsius and then dewatering the
solution to separate Mirabilite crystals.

2. A process in accordance with claim 1 wherein artificial cooling is employed and the brine prior to cooling step (c) is preconditioned according to the following steps:

5

(a) the brine is further evaporated until its specific gravity reaches between 1.30 and 1.32;

10

(b) the brine is dewatered to leave a salt slurry;

(c) the salt slurry is dissolved in water;

15

(d) the brine is cooled to between Zero and minus Five Degrees Celsius;

(e) the brine is dewatered to recover Mirabilite crystals.

20

3. A method of producing Thenardite including the processes of either claims 1 or claim 2 and the following further steps:

25

(a) washing the Mirabilite crystals with an appropriate washing liquor;

- (b) dewatering the resulting solution for solid/liquor separation and;
- (c) drying the solid recovered in the preceding step to produce Thenardite.

5

4. A method of producing Thenardite including the processes of either claims 1 or claim 2 and the following further steps:

10

(a) dissolving the Mirabilite by using hot steam;

15

(b) introducing a stoichiometric amount of Halite to the dissolved Mirabilite at a reaction temperature of between thirty eight and forty two Degrees Celsius;

20

(c) dewatering the reaction product for solid/liquor separation;

25

5. A process in accordance with claim 3 wherein Ethanol is added to the Mirabilate crystals in order to decrease the solubility of the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system and hence to increase Thenardite yield.

6. A method of producing Potassium Sulphate including the processes of either claims 1 or claim 2 and the following further steps:

5 (a) dissolution of the Mirabilite by introduction of hot steam;

10 (b) reacting a stoichiometric amount of KCl with the Mirabilite solution through continuous mixing for in excess of fifteen minutes at between thirty three and thirty seven Degrees Celsius;

15 (c) dewatering the product from the previous step to produce Glasserite crystals in NaCl base solution;

20 (d) reacting the Glasserite crystals with a stoichiometric amount of KCl in hot water through continuous mixing for in excess of twenty minutes between forty eight and fifty two Degrees Celsius;

25 (e) cooling the mixture from the previous step to between twenty and twenty five Degrees Celsius;

(f) dewatering the resulting NaCl base solution to recover K_2SO_4 crystals;

(g) drying the K_2SO_4 crystals to give stable Potassium Sulphate.

7. A method of producing Epsomite ($MgSO_4 \cdot 7H_2O$) using the processes of either of claims 1 or claim 2 and the following further steps:

(a) recovering the filtrate from the dewatering of the Mirabilite crystals and evaporating such bittern until a specific gravity of between 1.28 and 1.30 is reached so as to separate the Halite impurity;

(b) cooling the bittern to between zero and minus five Degrees Celsius;

(c) dewatering the bittern and recovering Epsomite crystals.

8. A method of producing Epsomite in accordance with claim 7 but including the following further steps:

(a) redissolving the Epsomite crystals obtained in step (c) of the preceeding claim in hot water;

5 (b) evaporating the resulting solution until it reaches a specific gravity of between 1.29 and 1.31;

10 (c) leaving the solution to gradually normalise at an ambient temperature of between twenty and twenty five Degrees Celsius;

15 (d) dewatering the solution to recover Epsomite crystals;

(e) drying the Epsomite crystals to form a stable product.

20 9. A method of producing Potassium Chloride comprising the following steps:

25 (a) performing the process steps defined in any one of claims 1, 2, 7 or 8 hereof up to at least the first dewatering step listed in said claims and then recovering the filtrate from one or more of the steps mentioned in said claims;

(b) subjecting said filtrate or filtrates from the dewatering of the Mirabilate or Epsomite slurries to evaporation until a specific gravity of between 1.35 and 1.37 is reached;

5

(c) slowly cooling the resulting bittern to a temperature of between twenty and twenty five Degrees Celsius;

10

(d) dewatering the bittern to recover a carnallite mixture;

15

(e) subjecting the carnallite solution to one or more flotations wherein air or Carbon Dioxide is bubbled through the solution;

20

(f) dewatering the flotation product to recover the Potassium Chloride crystals as a foam;

(g) drying the Potassium Chloride to produce a stable product.

25

10. A method of producing a Magnesium Hydroxide slurry ($\text{Mg}(\text{OH})_2$) comprising the steps of:

(a) performing the steps listed in claim 9.
hereof up to and including step (f)

5 (b) recovering the filtrate and diluting same
with fresh water until a specific gravity of
between 1.05 and 1.10 is achieved;

10 (c) reacting the diluted solution with Lime
(CaO) by rapid stirring ;

(d) thickening the solution by slow mixing;

15 (e) dewatering the product to recover the
Magnesium Hydroxide slurry product.

11. A method of producing Potassium Sulphate in
accordance with claim 6 wherein the Potassium
Chloride introduced at steps (b) and (d) is
20 manufactured in accordance with the method
described in claim 9 hereof..

25

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A. Arakel

12. A processing scheme for saline wastewater substantially as hereinbefore described with reference to the accompanying flow charts.

5 DATED this 8th day of January, 1993.

10 Aharon Vartan Arakel and
Donatus Katauskas by
their patent attorneys
Barker, Blenkinship &
Associates

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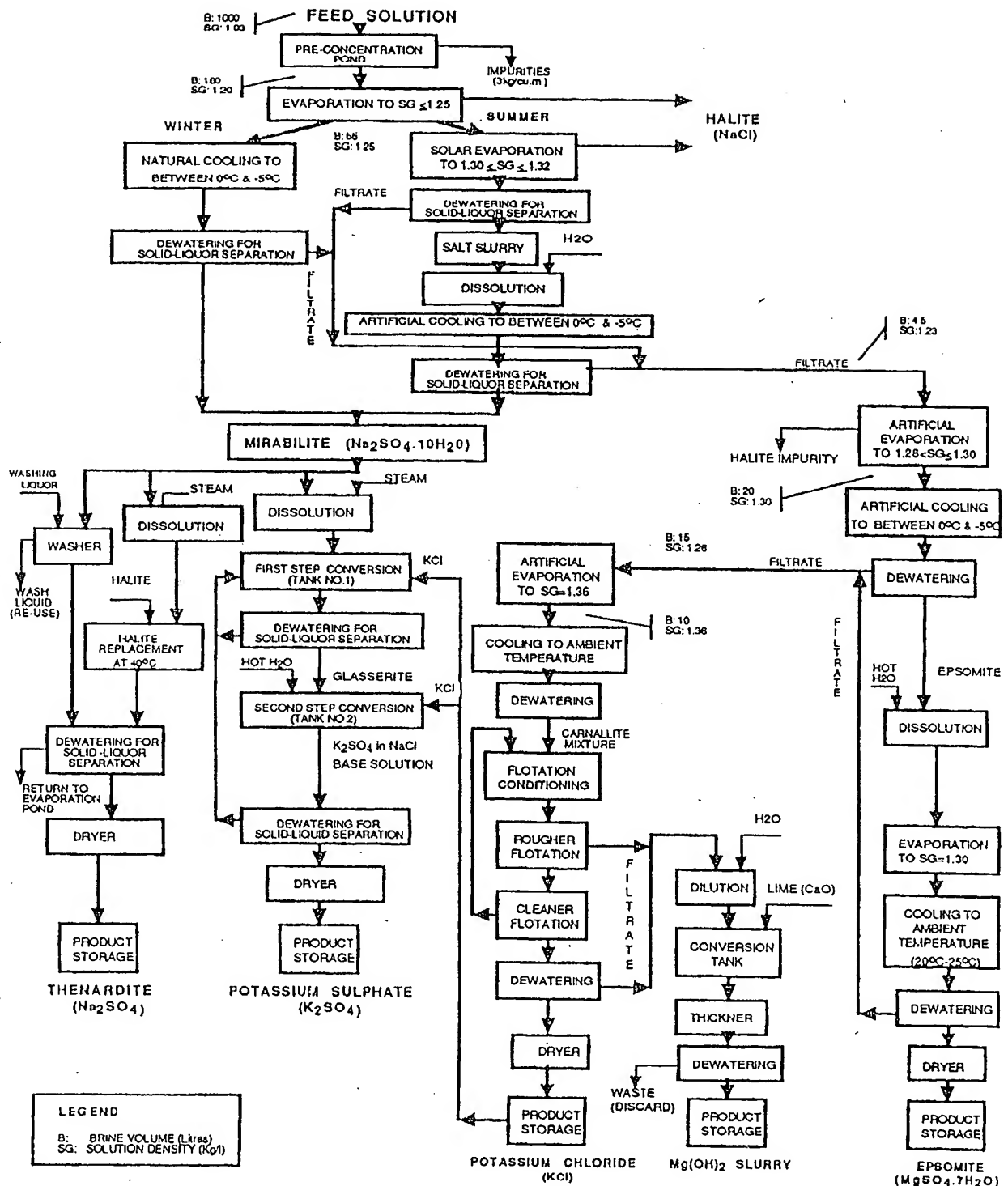


FIGURE 1. MASS FLOW BLOCK DIAGRAM FOR SALINE WASTEWATER PROCESS

MIRABILITE & THENARDITE

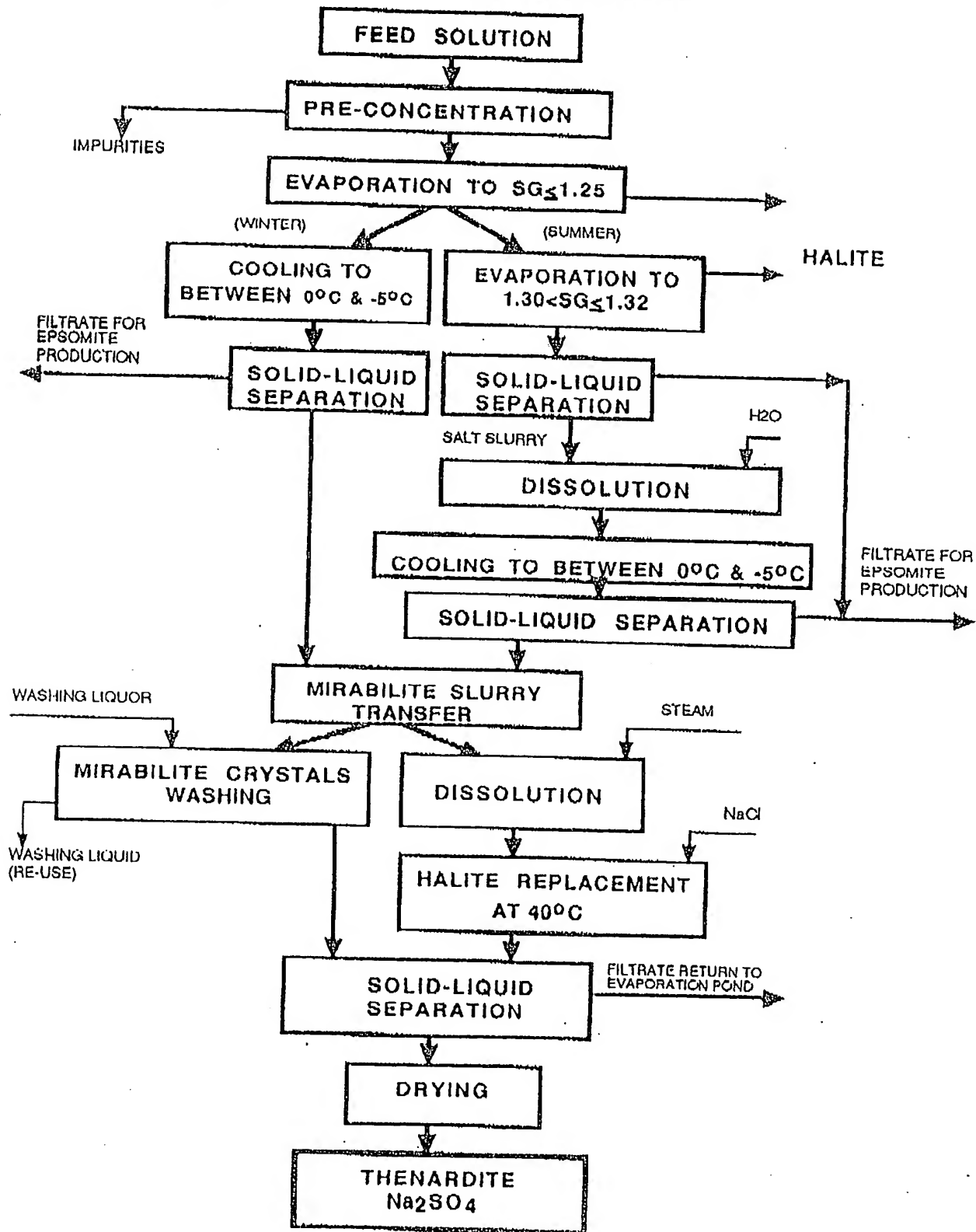


FIGURE 2.

POTASSIUM SULPHATE

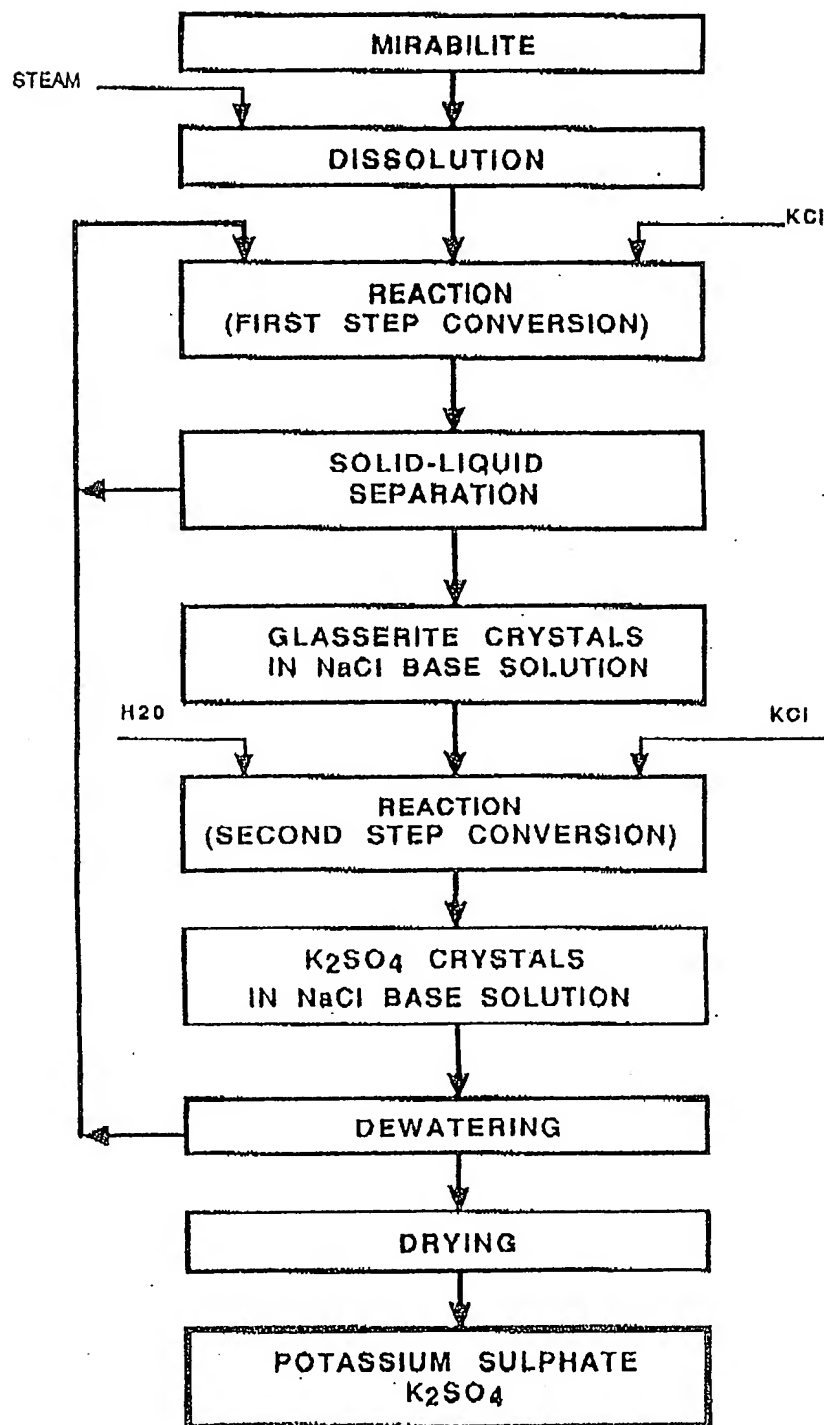


FIGURE 3.

POTASSIUM CHLORIDE

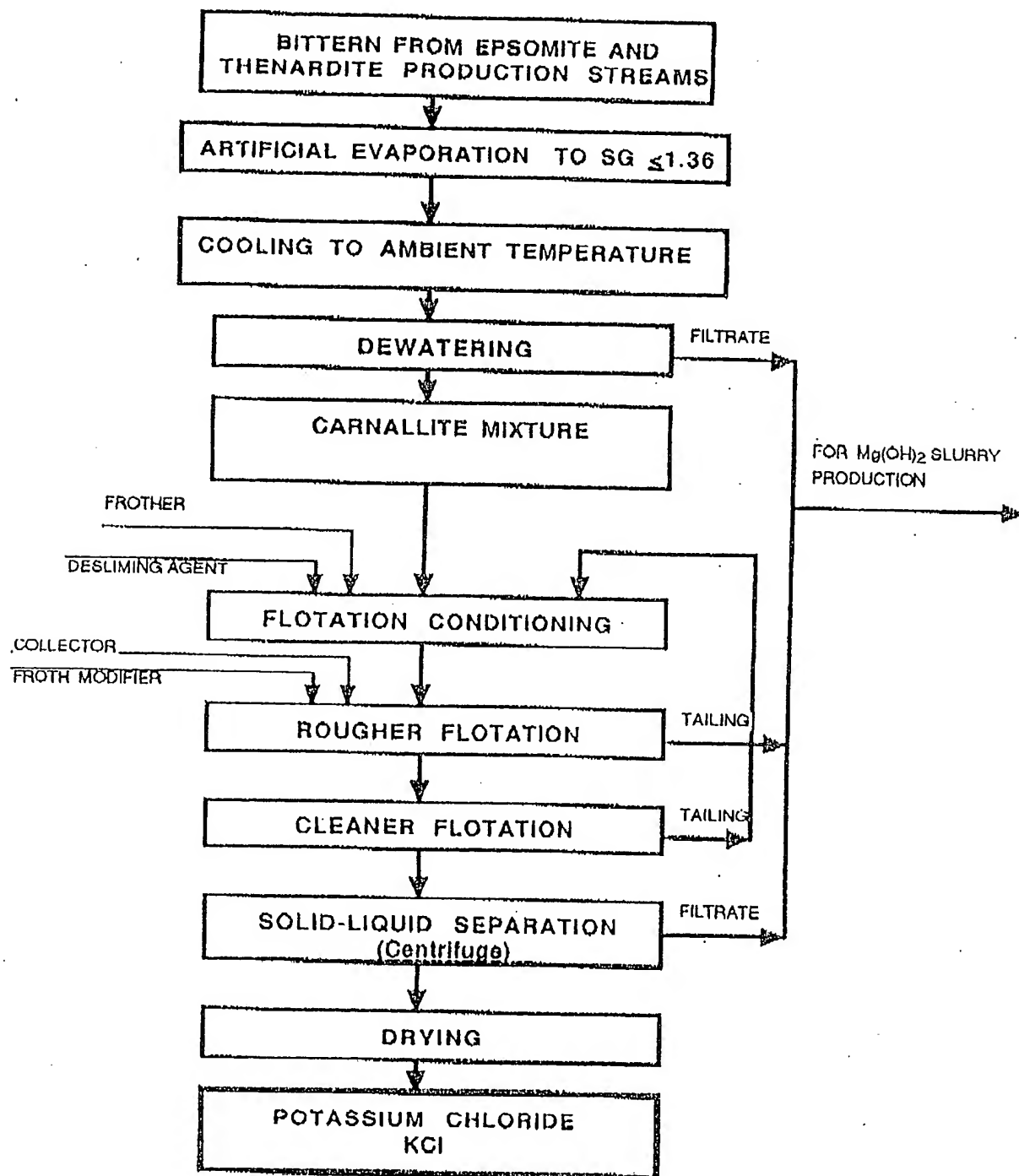


FIGURE 4.

EPSOMITE

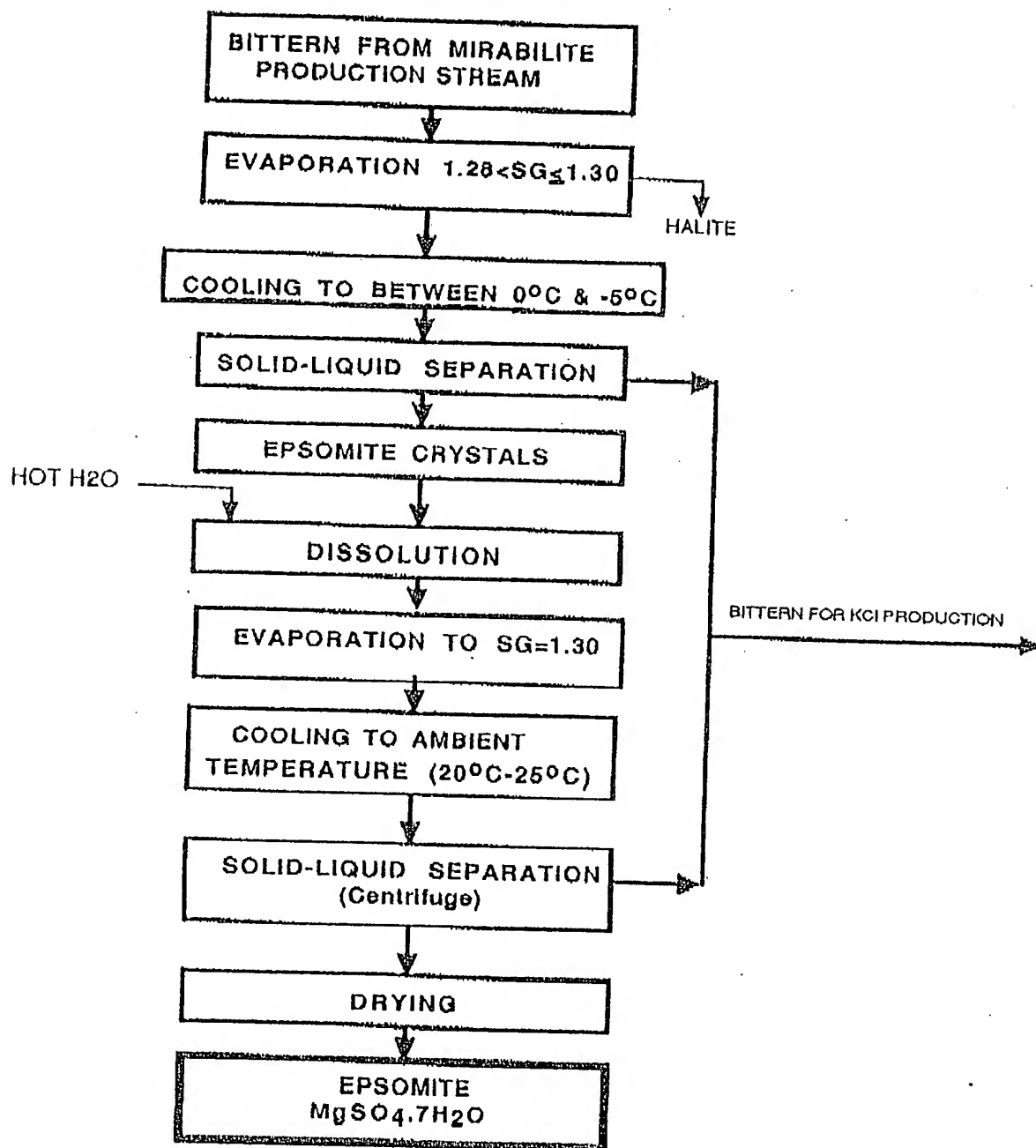


FIGURE 5.

MAGNESIUM HYDROXIDE SLURRY

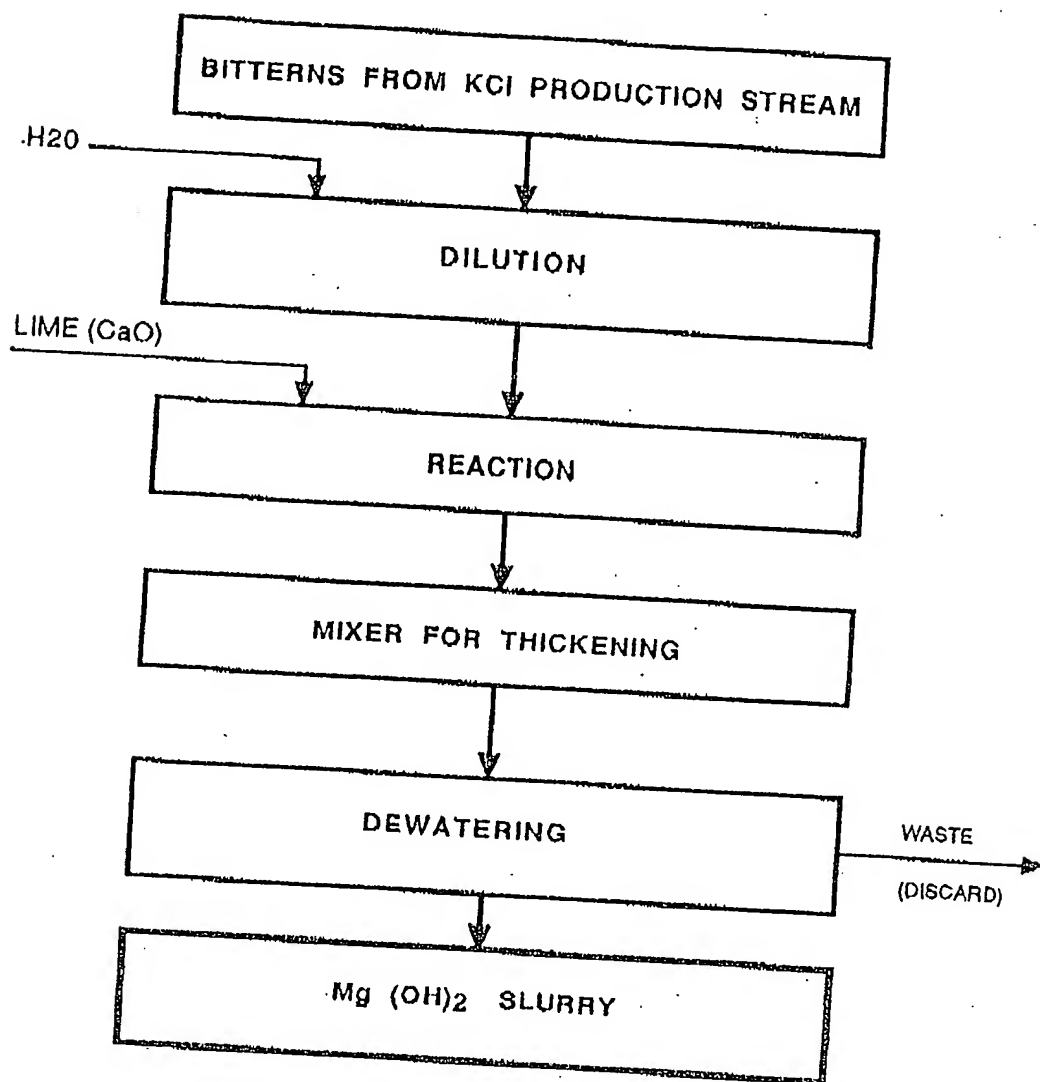


FIGURE 6.

FIGURE 7

THERMODYNAMIC REQUIREMENTS AND PROCESS STEPS FOR PRODUCTION OF VARIOUS PRODUCTS													
FINAL PRODUCT	FEED	SOURCE / STREAM	EVAPORATION (SG)	COOLING (TEMP. RANGE)	DIS-SOLUTION	DEWATERING (SOLID-LIQUID SEPARATION)	PROCESS STEPS						
							CONVERSION	FLOTATION	WASHING	DILUTION	DRYING	THICKENING	COMMENTS
HALITE (NaCl)	Mother Brine	Saline Wastewater	SG<1.25										
MIRABILITE (Na2SO4.10H2O)	Mother Brine	Saline Wastewater	1.30<SG<1.32	0°C to -5°C	Yes	Yes							Main product; no claim made
THEMARDITE (Na2SO4)	Mirabilite & Halite Products	Crystals from Mirabilite Production	1.30<SG<1.32	0°C to -5°C	Yes	Yes	Yes, with NaCl (optional)		Yes		Yes		Main product to recover Na & SO4
EPSOMITE (MgSO4.7H2O)	Mother Brine	Filtrate from Mirabilite Production	1.28<SG<1.30 1.29<SG<1.31	0°C to -5°C 20°C to 25°C	Yes	Yes					Yes		Main product to recover Na & SO4
POTASSIUM CHLORIDE (KCl)	Bittern	Filtrate from Mirabilite & Epsumite Production	1.35<SG<1.37	20°C to 25°C		Yes		Yes					Main product to recover Mg & SO4
POTASSIUM SULPHATE (K2SO4)	Mirabilite & KCl Products	Crystals from KCl & Mirabilite Production	1.25<SG<1.32	0°C to -5°C	Yes	Yes	Yes, with KCl & H2O				Yes		Main product to recover K and Cl
MAGNESIUM HYDROXIDE Mg(OH)2 SLURRY	Bittern & Lime (CaO)	Filtrate from KCl Production and Lime From External Source		20°C to 25°C		Yes	Yes, with Lime		Yes			Yes	Secondary product for Value Adding

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